Single-Particle Diffusion-Coefficient on Surfaces with Ehrlich-Schwoebel-Barriers

K. Mussawisade, T. Wichmann and K.W. Kehr

Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

Abstract

The diffusion coefficient of single particles in the presence of Ehrlich-Schwoebel barriers (ESB)is considered. An exact expression is given for the diffusion coefficient on linear chains with random arrangements of ESB. The results are extended to surfaces having ESB with uniform extension in one or both directions. All results are verified by Monte Carlo simulations.

I. INTRODUCTION

Diffusion of particles on stepped surfaces is of great current interest. Stepped surfaces occur in the form of more or less regular terraces on vicinal surfaces, or in the process of island formation. Ehrlich and Schwoebel [1,2] pointed out the existence and importance of what are now called Ehrlich-Schwoebel barriers. A particle which diffuses on a higher terrace of a stepped surface experiences a higher than normal barrier at the edge of the terrace while a particle on the lower terrace experiences a lowered site energy when approaching the step edge. In this paper the diffusion coefficient of single particles on surfaces with one- and two-dimensional arrangements of Ehrlich-Schwoebel barriers will be calculated.

In previous papers [7,8] the diffusion coefficient of a particle in a one-dimensional periodic arrangement of Ehrlich-Schwoebel barriers has been derived. In Ref. [8] also the collective diffusion coefficient of a finite concentration of particles in periodic arrangements of Ehrlich-

Schwoebel barriers has been calculated in a mean-field approximation. We will present results for single-particle diffusion that are valid for disordered arrangements of such barriers. Our derivations have been made possible by recent progress in the theory of diffusion in disordered lattices [4–6]. An exact result for the diffusion coefficient of a particle on a linear chain with rather general transition rates is now available and will be described in the following section. This result can be applied to the case of Ehrlich-Schwoebel barriers and allows for a simple and exact treatment of both ordered and disordered arrangements of the barriers. An important point is the extension to two-dimensional surfaces which will be done in Sec.III. The final section contains concluding remarks.

II. DIFFUSION COEFFICIENT ON LINEAR CHAINS WITH EHRLICH-SCHWOEBEL-BARRIERS

The asymptotic behavior of the mean-square displacement of independent particles is characterized by a diffusion coefficient which is given for linear chains with rather arbitrary transition rates by ([4–6])

$$D = \left\{ \frac{1}{\rho_i \Gamma_{ij}} \right\}^{-1} . \tag{1}$$

ρ_i is the thermal occupation factor of site i, Γ_{ij} the transition rate from site i to site j, and the lattice constant has been set unity. The curly brackets designate the disorder average which has to be taken over the distributions of the site and barrier energies. The thermal occupation factors are defined by

$$\rho_i = \frac{\exp(-\beta E_i)}{\{\exp(-\beta E_i)\}} \tag{2}$$

where E_i is the energy of site i. The transition rates are given by an Arrhenius expression,

$$\Gamma_{ij} = \Gamma_0 \exp(-\beta(E_{ij} - E_i)) \tag{3}$$

where E_{ij} is the energy barrier between site i and site j, and β is the inverse temperature (i.e. $\beta = 1/k_B T$). The site energies E_i , counted from a common origin, shall always be

nonpositive while the barrier energies E_{ij} are assumed to be nonnegative. In this way all transition rates fulfill $\Gamma_{ij} \leq \Gamma_0$. We emphasize that the expression (1) for the diffusion coefficient is only valid for systems which have a unique equilibrium state in the limit of number of sites $N \rightarrow \infty$; otherwise the thermal occupation factors ρ_i are not defined.

The Ehrlich-Schwoebel barriers (ESB), which have been postulated from experimental observations, are of the type where Eq.(1) is applicable. A pictorial representation of ESB on a linear chain is given in Fig.I in the form of a 1-dimensional potential landscape. The potential has to transcribed to transition rates by application of the Arrhenius expression (3). According to Eq.(1) an average over the inverse of weighted transition rates has to be performed. Multiplying the occupation factors (2) with the rates (3) one observes a cancellation of the factors $\exp(-\beta E_i)$. An effective factorization of the expression results and it reads

$$D = \left\{ \frac{1}{\exp(-\beta E_i)} \right\}_{E_i}^{-1} \left\{ \frac{1}{\exp(-\beta E_{ij})} \right\}_{E_{ij}}^{-1}, \tag{4}$$

Now the diffusion coefficient of a particle on a chain with randomly distributed ESB of identical heights and depths (see Fig 1) is easily calculated,

$$D = \frac{1}{\left(1 - c_s + c_s \exp(\beta E_s)\right)\left(1 - c_s + c_s \exp(-\beta E_t)\right)} \tag{5}$$

where c_s is the concentration of the ESB, E_s the height of the ESB and E_t the energy of the site at a surface step. The result (5) is equivalent to the results derived in [7] and [8]. The authors of [7] and [8] consider regularly stepped surfaces i.e. the length L between two steps is always constant. In our result the diffusion coefficient only depends on the concentration c_s of the ESB and L need not to be constant, i.e. $c_s = 1/\{L\}$ where $\{L\}$ is the average distance of the barriers.

In (FIG 2.) one recognizes good agreement of Monte Carlo results for particle diffusion on such chains with the diffusion coefficient as given in Eq. (5).

A comment on the absence of directional effects in the diffusion coefficient on linear chains with ESB is in order. Since the diffusion coefficient of the linear chain with ESB has

the factorized form eq.(4), the arrangements of the high barriers and the deep sites does not matter for the magnitude of it. This seems to contradict the idea that the ESB prevent particles from flowing from higher terraces to lower ones. We point out that we derive the diffusion coefficient of single, independent particles, which does not exhibit any directional effects (see also [7,9]). In the linear-response regime the mean flux of single particles up and down the steps is the same for a given small bias. The ESB become effective for the formation of islands, if there are several particles present on the highest terrace. If one particle is kept next to a high barrier at the terrace edge, a second particle may attach to this particle, and so on, leading eventually to the formation of a higher terrace.

In the paper Ref. [8] collective diffusion on stepped surfaces with ESB was considered for lattice gases with exclusion of double occupancy. No further interactions of the particles were considered. The formula Eq.(4) in [8] for D_{xx} agrees in the limit $c \to 0$ with the previous result [7] and our result. The limiting behavior for $c \to 1$ can be directly studied by our methods. The problem is then equivalent to a single-vacancy diffusion problem where the transition rates *into* the sites are given [10]. Application of Eq.(1) leads to

$$D(c \to 1) = [(1 - c_s + c_s \exp(-E_t))((1 - c_s + c_s \exp(\beta(E_t + E_s)) + c_s \exp(\beta E_t))]^{-1} \qquad (6)$$

The expression given in [8] gives an interpolation between $c = 0$ and $c = 1$ and approaches for $c \to 1$ the result Eq.(6). We emphasize that in the site-exclusion lattice-gas model which was used in [8] additional interactions of the particles are neglected. Interaction effects of the particles are expected to be important for real surfaces, hence the applicability of the formulae to real systems needs careful examination.

III. DIFFUSION COEFFICIENT ON TWO-DIMENSIONAL SURFACES

The theory of diffusion in the presence of ESB can be extended to two-dimensional surfaces under the assumption that the random walk of the particle(s) can be considered as independent in the two surface directions. There are two cases where this condition is fulfilled:

a) *Terraces with infinite uniform extension in one direction*

This case is of practical interest because vicinal surfaces may have steps which extend uniformly in the direction perpendicular to the steps. See Fig.3 for a pictorial representation. Clearly the random walk of a particle in the x- and y-directions can be considered as independent. While the particle experiences ESB barriers when it performs random walk in the x-direction, it can make jumps in the y-direction with a uniform, site-independent transition rate Γ. The summary diffusion coefficient is then given by

$$D = \frac{1}{2}(D_x + D_y) \ . \tag{7}$$

The quantity D_x is given by (1) while D_y is simply $D_y = \Gamma$ when the lattice constant is set unity. Fig.4 shows the result of simulations for such a 2-dimensional model, together with the predictions of Eq.(7). One notices complete agreement of theory and simulations.

In Ref. [7] also the case was considered where the transition rates between the sites with lowered energies at the edge of the terrace, in y-direction, have a smaller value, Γ_2. The result for the perpendicular diffusion coefficient D_y is then a superposition of the contributions of the different rows in y-direction. The result of [7] for D_y is easily extended to the case of varying terrace distances L.

b) *Independent uniform terraces in x and y directions.*

If there are independent uniform terraces in x and y direction, for example as indicated in Fig.5, the diffusion coefficient may again be calculated by applying the principle of independent random walks in the two directions. It is assumed that ESB exist at the terrace steps in each direction. The diffusion coefficient D is again obtained from the superposition Eq.(7), but now D_y is also given by the result Eq.(5). Figure 6 demonstrates the verification of the analytical result by numerical simulations.

IV. CONCLUDING REMARKS

We have derived the diffusion coefficient of single particles on linear chains with random arrangements of ESB. We could extend the results to two-dimensional surfaces with terraces

and associated ESB with infinite uniform extension in one or two directions. All results were validated by Monte Carlo simulations. Recently also the necessity of introducing more complicated barriers at the step edges, than the conventional ESB, has been pointed out [11]. The derivation of the diffusion coefficient for such barrier structures from our Eq. (1) is straight forward. One open problem is the treatment of diffusion of single particles on terraces which do not extend straightly in the perpendicular direction, i.e., terraces with kinks or more complicated defects. On stepped surfaces the diffusion can only be separated in contributions of each direction if the probability of a jump parallel to the steps does not depend on the position of the particle regarding to the steps. Thus the single-particle diffusion coefficient is not yet known for more complicated forms of terraces. Another unsolved problem is the diffusion coefficient of many interacting particles which obey site exclusion (i.e., interacting lattice gases), on stepped surfaces with ESB. The solution of this problem would be important for an analytic understanding of ,e.g., island growth.

We thank J. Krug, T. Michely and M. Rost for discussions.

REFERENCES

[1] G. Ehrlich, F.G. Hudda, J. Chem. Phys. **44** (1966) 1039

[2] R. L. Schwoebel, E. J. Shipsey, J. Appl. Phys. **37** (1966) 3682

[3] R. L. Schwoebel, J. Appl. Phys. **40** (1969) 614

[4] K. Mussawisade, T. Wichmann, K. W. Kehr, J. Phys. Condens. Matter **9** (1997) 1181

[5] R. Kutner, Physica A **224** (1996) 558

[6] R. Kutner, D. Knödler, P. Pendzig, R. Przenioslo, and W. Dieterich in "*Diffusion Processes: Experiment, Theory, Simulations*" edited by A. Pekalski, Lecture Notes in Physics **438** (Springer, Berlin, 1994), p. 197.

[7] A. Natori, R. W. Godby, Phys. Rev. B **47** (1992) 15816

[8] J. Merikoski, S. Ying, Surface Science **381** (1997) L623

[9] K.W. Kehr, K. Mussawisade, T. Wichmann, and W. Dieterich, Phys.Rev.E., in print

[10] K.W. Kehr, O. Paetzold, and T. Wichmann, Phys.Lett.A **182** (1993) 135

[11] K. Kyuno, G. Ehrlich, Surface Science **383** (1997) L766

Figure Captions

FIG. 1. Ehrlich-Schwoebel barriers

FIG. 2. Diffusion coefficient of a particle vs. concentration of the barriers for different Temperatures in the 1-dimensional case. Lines: exact calculation. Points Monte Carlo Simulations.

FIG. 3 Ehrlich-Schwoebel barriers extended to two dimensions.

FIG. 4. Diffusion coefficient of a particle vs. concentration of the barriers for different Temperatures in the 2-dimensional case where the terraces are uniformly extended in the y-direction. Lines: exact calculation. Points Monte Carlo Simulations.

FIG. 5 Ehrlich-Schwoebel barriers in both x and y-directions.

FIG. 6 Diffusion coefficient of a particle vs. concentration of the barriers in the 2-dimensional case where in both x and y-directions barriers occur (cf. Fig. 5). Lines: exact calculation for different Temperatures. Points: Monte Carlo Simulations.

FIGURES

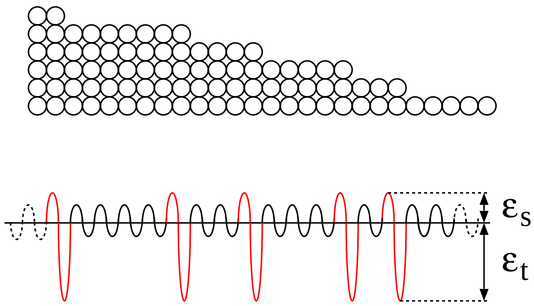

FIG. 1.

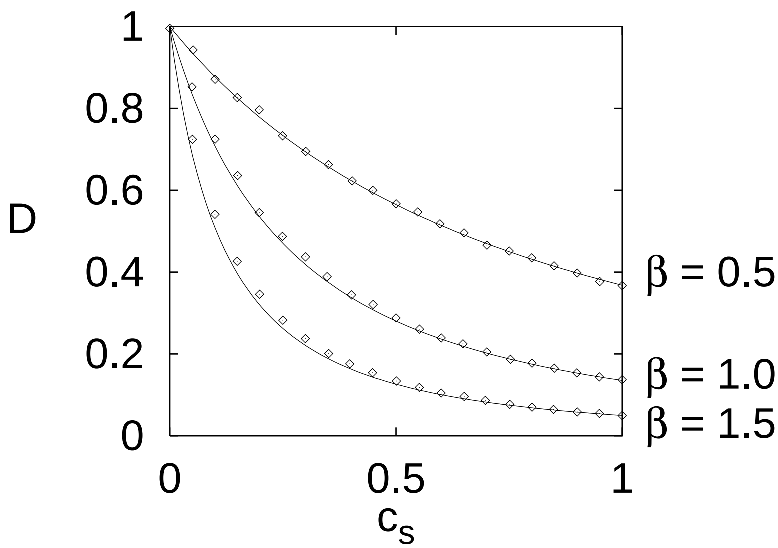

FIG. 2.

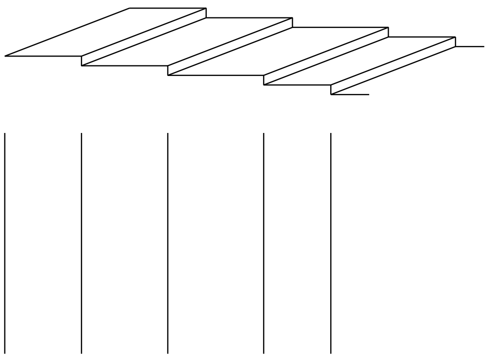

FIG. 3.

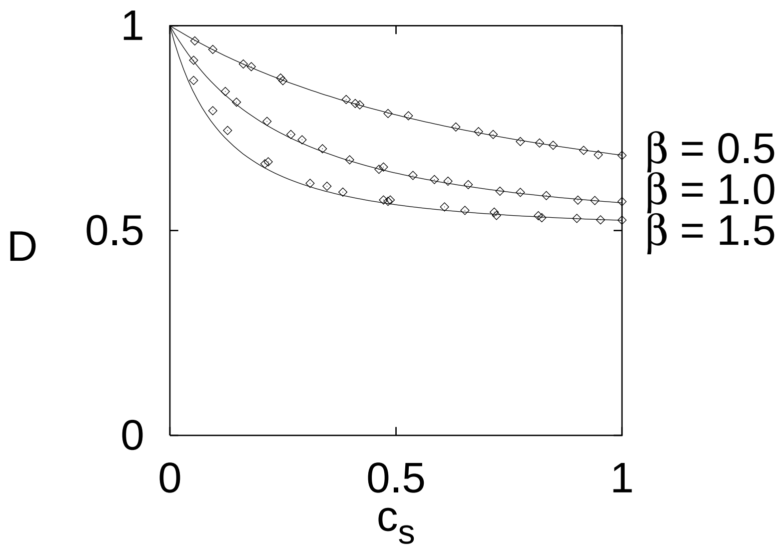

FIG. 4.

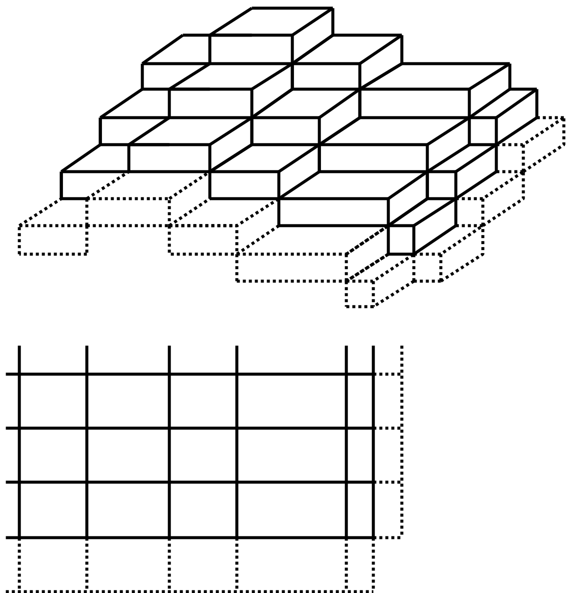

FIG. 5.

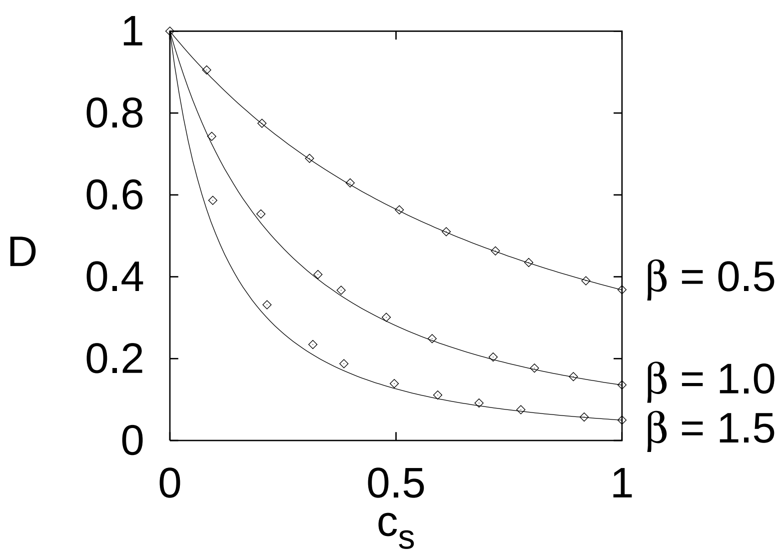

FIG. 6.